Periodicity and thickness effects in the cross section of quantum well states

A. Mugarza,[1] J. E. Ortega,[1] A. Mascaraque,[2] E. G. Michel,[2] K. N. Altmann,[3] and F. J. Himpsel[3]
[1]*Donostia International Physics Center and Centro Mixto de Materiales CSIC-UPV, Departamento de Física Aplicada I, Universidad del País Vasco, Plaza de Oñate 2, 20018-San Sebastián, Spain*
[2]*Instituto ''Nicolás Cabrera'', Departamento de Física de la Materia Condensada, C-III Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain*
[3]*Physics Department, University of Madison Wisconsin, 1150 University Avenue, Madison, Wisconsin 53706-1390*
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The photoemission cross section of quantum well states in very thin Cu films has been analyzed as a function of photon energy within a wide energy range. We show that this cross section is periodical in k space, peaking around vertical transitions of the respective Cu bulk band. The cross section peak width is analyzed in terms of final- and initial-state wave vector broadening. The latter can only be detected at low kinetic energies due to reduction of final state broadening. The initial state $k_\perp$ broadening increases when the Cu film gets thinner, as simply expected from the uncertainty principle.

In a thin metal film deposited on a solid substrate electrons are confined in the perpendicular direction by the surface and interface potentials, leading to the formation of quantum well (QW) states. These are known to be responsible of intriguing phenomena in layered systems, like the oscillatory magnetic coupling of two magnetic layers across a nonmagnetic spacer[1] or the giant magnetoresistance.[2] Their existence has been frequently probed in noble and transition metals by means of angle-resolved photoemission[3] (ARPES) where they display strong energy-dependent cross sections. In general the QW cross section is expected to be maximum near vertical transitions of the bulk crystal of the material comprising the thin film. This reflects the conservation of the perpendicular wave vector in transitions from thin film states to final states in the continuum.[4] Such behavior has been qualitatively observed in Cu/Co(100) (Ref. 5) and Ag/Cu(111) (Ref. 6). Away from this vertical transition region one can also obtain periodic modulations of the QW intensity. They have been attributed to discretization of the photoemission final-state band,[6] but also to surface-interface coherent photoemission effects.[7,8] Furthermore, it has been claimed that at low energies and very thin films such emission dominates over the regular QW photoemission from inside the thin film.[8] Here we show that this is not true for Cu films on Co(100), since the cross section displays clear peaks around vertical transitions to the lowest three bulk final-state bands. The cross-section peak width is analyzed in terms of perpendicular wave vector broadening ($\Delta k_\perp$) for both final and initial (i.e., QW) states. The results show that the final-state $\Delta k_\perp$ dominates at $h\nu \sim 80$ eV, whereas at $h\nu \sim 14$ eV initial-state effects are necessary to explain the width of the transition peak. The thickness dependence of the initial state $\Delta k_\perp$ and its magnitude appears to be related to confinement within the QW via the uncertainty principle.

High-resolution photoemission experiments were done at the Synchrotron Radiation Center in Stoughton, Wisconsin ($h\nu < 16$ eV) and at the VUV photoemission beam line of the synchrotron radiation laboratory Elettra at Trieste, Italy ($h\nu > 40$ eV). In both cases the polarization of the synchrotron light was set to p-like in order to enhance sensitivity to Δ_1-symmetry initial states. The photoemission spectra were normalized to the photon flux. The Cu(100) surface was electrochemically polished prior to the *in situ* sputter-annealing cycles.[1] After substrate preparation, a 10 monolayer (ML) thick Co film was grown, and immediately on top of this film Cu was deposited. Both Co and Cu were evaporated from electron-beam-heated sources onto the Cu(100) substrate held at 300 K, with a deposition rate of ~ 1 Å/min determined with a quartz microbalance. Epitaxial growth and film quality was controlled by low-energy electron diffraction (LEED), which always displayed very low background and sharp spots. The characteristic QW features for every integral layer allowed further calibration of the Cu thickness.

The valence band photoemission spectra in Figs. 1 and 2 show the QW-state valence band spectra for a 3 ML and a 6 ML Cu film, respectively, at different photon energies (the numbering follows Ref. 3). In contrast to other QW resonances near E_F,[9] both $n=2$ for 3 ML (at $E-E_F=-0.9$ eV) and $n=3$ for 6 ML (at $E-E_F=-1.2$ eV) states display no appreciable dispersion. They are truly two-dimensional spin-down states, totally confined by Bragg reflection at the Co minority gap.[3] The peaks appear broadened due to emission from smaller patches of the surface with ± 1 ML thickness. This is more evident in the left panel of Fig. 2, i.e. at lower energies. Although the main feature still corresponds to the $n=2$ QW state of 3 ML, the high-energy resolution allows to distinguish from up to 4 different levels. The lack of lateral uniformity in the growing film appears to be characteristic of the room-temperature (RT) evaporated films, since it persists for nominally complete layers. The QW intensity varies strongly in the wide photon energy range studied, i.e., the range of vertical transitions to final states in the second, third, and fourth branches of the Δ_1 bulk band. At the lower energy transition the strong energy-dependent cross section washes away QW features in the range of just a few eV. This effect, and the presence of QW peaks from patches with different thicknesses, makes it difficult to provide an accurate coverage determination. Indeed the relative peak intensities are dramatically affected by the

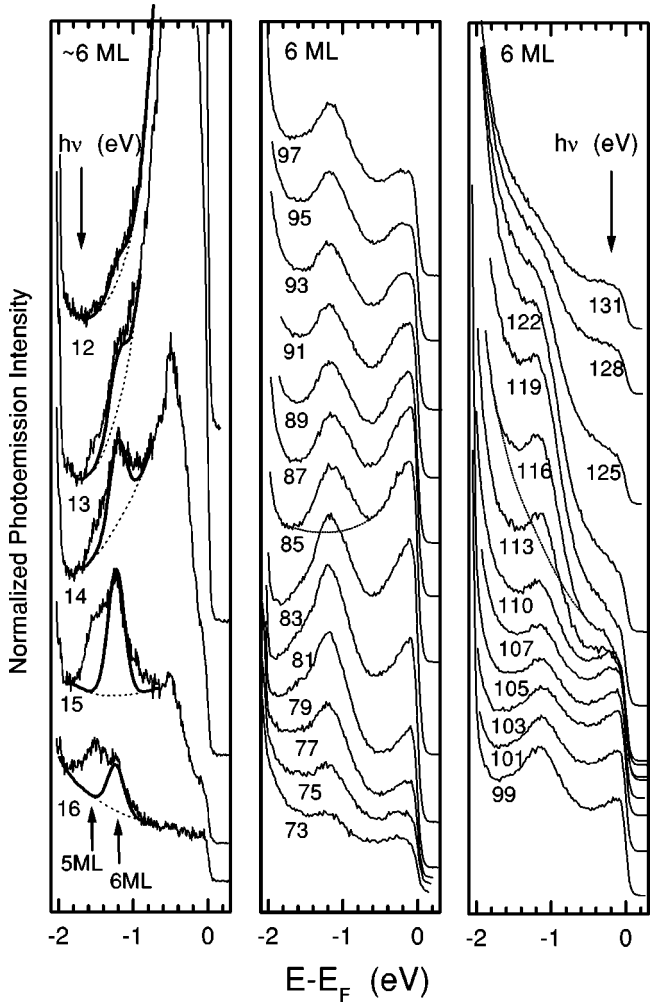

FIG. 1. Photoemission spectra as a function of the photon energy for a 6 ML Cu film showing the $n=3$ minority spin QW state. A smaller 5.0 ML QW peak is better distinguished in the lower energy spectra. In that case the thick line represents a Gaussian fit to the $n=3$ peak for 6.0 ML. The dotted lines are typical backgrounds used to determine the area under the peak (see Fig. 3).

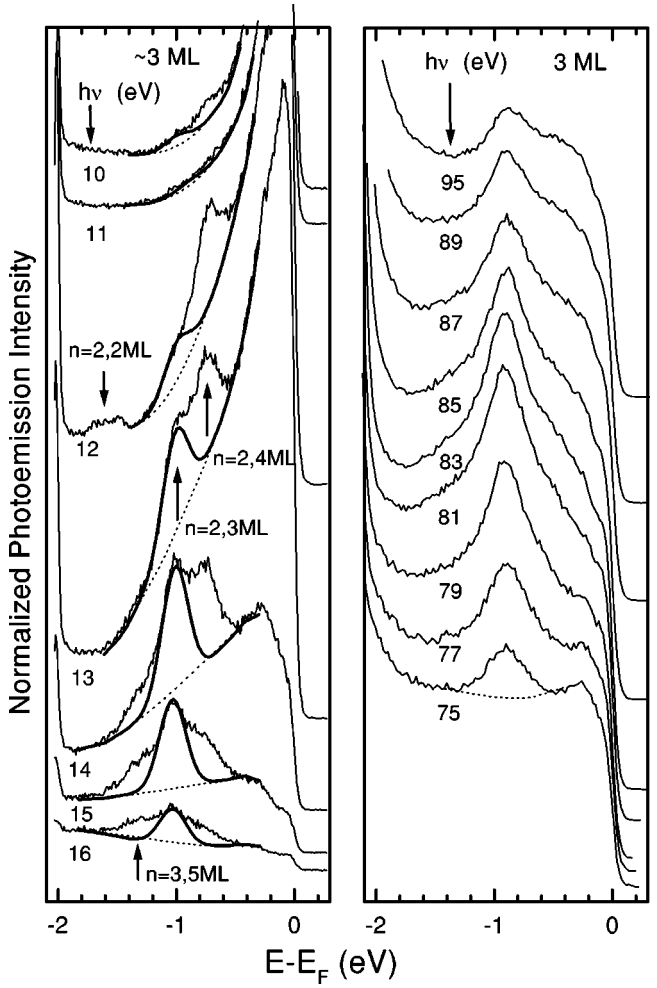

FIG. 2. Photoemission spectra at several photon energies for a 3 ML Cu film. Although the 3 ML QW state peak is dominant, we detect again emission from locally different thickness at low energy. The thick lines represent Gaussian fits to the 3.0 ML peak.

cross section change within 1 eV photon energy. In this case we separate the specific layer contribution by performing a Gaussian fitting. The resulting peak for 3.0 ML and 6.0 ML is marked in Figs. 1 and 2 with a thick line. On the other hand, this sharp $k_\perp$ resonance in the cross section enhances the QW peak intensity. This fact, together with a better photon and electron energy resolution, makes the low-energy regime the optimum for QW state studies.

In Fig. 3 we have plotted the peak intensity as a function of the photon energy. The intensity is defined as the area under the QW peak in the spectra of Figs. 1 and 2, after subtraction of a smooth background. As an example, we include in Figs. 1 and 2 the background lines used for some spectra. For the low-energy range, the area is that of the Gaussian fit to the 3.0 ML and the 6.0 ML peaks indicated with thicker lines. The error in the data is plotted jointly and is mostly determined by the election of the background line. The cross section maxima appear at 14.6 eV, 81 eV, and 119 eV for 6 ML, whereas for 3 ML intensity maxima are found at 13.8 eV and 82 eV. The higher-energy transition has not been studied in the latter case. Away from the energy range shown in Fig. 3, the intensity of the QW peak decreases strongly.

The photon energy scale is converted on top of Fig. 3 into a final-state (reduced) wave vector scale assuming photoemission final-state bands as in bulk Cu. Strictly speaking, the final state should be defined as a mixed Co/Cu state. However, due to the finite escape depth this fact is only important for thin films and low energies (around 14 eV), where the electron inelastic mean free path is of the order of 8 atomic layers. Even in this case, since both Co and Cu share a very similar band structure for energies above E_F+10 eV,[9] the deviation from the the electronic structure of bulk Cu is expected to be small.[10] Thus we can assume Cu-like final-state bands. At higher energies these are properly represented by a free-electron-like parabola calculated with an inner potential $V_0-E_F=-7.2$ eV.[11] The lower-energy band is taken from the experimental data of Ref. 12. With respect to $k_\perp$, the cross section is periodic, i.e., all transitions occur at the same value $k_\perp \sim 0.75(2\pi/a)$ for 3.0 ML and $k_\perp \sim 0.74(2\pi/a)$ for 6.0 ML.[13] Such a periodic variation in the bulk Brillouin zone is directly related to the properties of the QW-state wave function in the perpendicular direction. It is analogous to the case of surface states, where the intensity

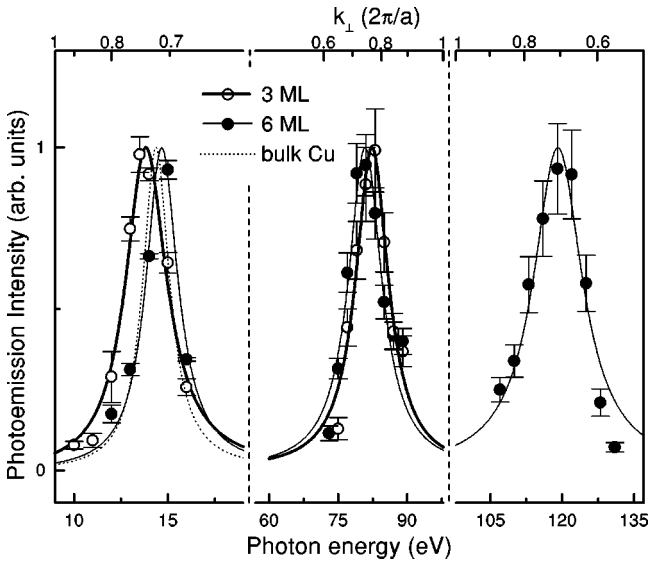

FIG. 3. Photoemission intensity variation of the 6 ML (thin line, dots) and the 3 ML (thick line, circles) QW states of Cu(100) films. The lines are Lorentzian fits to the data points. At low energy we include the Lorentzian fit to a constant-initial-state curve for bulk Cu (dotted line).

peaks at the fundamental frequency of the Fourier spectrum in the vertical direction, i.e., k_{edge} in the bulk Brillouin zone.[14] In QW states $k_\perp$ can be deduced from the envelope function model.[15] In this model the wave function is made up with a Bloch-like rapid oscillation derived from the closest bulk band edge ($k_{edge}=2\pi/a$), modulated by an envelope function ($k_{env}=2\pi/d$) that allows the boundary conditions to be met at both the surface and the interface. If we neglect changes in the bonding near the interfaces, the total wave vector $k_\perp(E)=k_{edge}\pm k_{env}$ follows the dispersion of the bulk (s,p) band. This allows us to locate the QW state within the bulk Brillouin zone in the perpendicular direction. Assuming the lower initial-state (s,p) band given in Ref. 12, we obtain $k_\perp\sim 0.77(2\pi/a)$ for 3.0 ML and $k_\perp\sim 0.75(2\pi/a)$ for 6.0 ML, in fair agreement with the results obtained in Fig. 3.[16] Note that the envelope function model accounts for the periodic variation of the potential within the film via the Bloch oscillation k_{edge}. Assuming only surface and interface discontinuities in the potential to calculate the photoemission matrix element one cannot explain the periodicity shown in Fig. 3.[8] Thus in our case the inner corrugation of the film cannot be neglected, even for the thinnest one.

Optical transitions can be described in the momentum space using complex perpendicular wave vectors $k_\perp=k_\perp^R+ik_\perp^I$ for the initial state (i) and the final state (f).[17] In this way, the cross section can be thought of as the $k_\perp$ convolution of two Lorentzians, where the imaginary part of $k_\perp$ is the Lorentzian broadening. The curves in Fig. 3 can be regarded as intensity scans in the constant-initial-state (CIS) photoemission mode. Since final states are extended we can define the group velocity $\hbar v_f=\partial E/\partial k_\perp$ and then write[17]

$$\frac{\Gamma_m}{\hbar}\frac{1}{v_f}=\Delta k_{\perp,i}+\Delta k_{\perp,f}, \tag{1}$$

where Γ_m stands for the measured cross section peak width and $\Delta k_\perp=2k_\perp^I$. In Table I the experimental widths [full width at half maximum (FWHM)] Γ_m obtained for the different peaks are summarized. We include data for 4.0 ML and 5.0 ML determined from the spectra on the left panels in Figs. 1 and 2, as well as a fit obtained for bulk Cu at lower energy (dotted line in Fig. 3). We note that peak widths are very similar for 3 ML and 6 ML in the second resonance at ~ 80 eV, but Γ_m decreases as we go from 3.0 ML to 6.0 ML and to bulk Cu at the ~ 14 eV resonance.

Based in Eq. (1) we can interpret the experimental width of the cross section curve in terms of initial- and final-state wave vector broadening. To this end in Table I we compare Γ_m/v_f with $\Delta k_{\perp,f}$. At high energies v_f can be assumed to be constant in the energy range Γ_m defined by the peak width. It is readily obtained from the free-electron-like final-state band mentioned before. For the lower resonance, the final-state band is close to the X_1 point, where v_f changes much faster as a function of the energy. In order to fit the data in this case, $v_f(E)$ is obtained from the parabolic band given in Ref. 12 and it is already introduced as a correction to the experimental Lorentzian fit in Fig. 3. $\Delta k_{\perp,f}$ in Table I is defined as the inverse of the photoelectron escape depth, which in turn is estimated from the experimental inelastic mean free path (IMFP) for bulk Cu.[12]

At the higher-energy transition around ~ 80 eV $\Delta k_{\perp,f}$ is similar to $\Gamma_m/(\hbar v_f)$. Thus in this case the final-state broadening appears to shade the initial state broadening contribution. This is also supported by the fact that there is no difference in $\Gamma_m/(\hbar v_f)$ from 3.0 ML to 6.0 ML. In contrast,

TABLE I. Experimental cross section linewidths and the corresponding initial- and final-state $\Delta k_\perp$ for the 6 ML and the 3 ML QW states at two different energy ranges (see the text). For the low-energy regime data for 4 ML ($n=2$ state) and 5 ML ($n=3$ state) have been included. IMFP data for final-state broadening and v_f values have been taken from Ref. 12.

	Thickness (ML)	Γ_m (ev)	$\Gamma_m/\hbar v_f$ (Å^{-1})	Δk_f (Å^{-1})	Δk_i (Å^{-1})
$h\nu\sim 82$ eV	3	8.7 ± 0.9	0.23 ± 0.05	0.250	
	6	9 ± 1	0.24 ± 0.03	0.250	
$h\nu\sim 14$ eV	3	2.7 ± 0.2	0.15 ± 0.01	0.07	0.08 ± 0.01
	4	3.1 ± 0.6	0.18 ± 0.03	0.06	0.12 ± 0.03
	5	2.2 ± 0.1	0.12 ± 0.02	0.09	0.04 ± 0.02
	6	2.1 ± 0.3	0.11 ± 0.02	0.07	0.03 ± 0.02
	Bulk Cu	1.7 ± 0.5	0.09 ± 0.03	0.07	0.02 ± 0.03

$\Gamma_m/(\hbar v_f)$ increases by 35% from 6 ML to 3 ML at the lower-energy resonance. At around 14 eV the IMFP goes up to 15 Å in Cu,[12] i.e., Δk_f is reduced to 0.07 $Å^{-1}$, about half of the value of $\Gamma_m/(\hbar v_f)$. Therefore Δk_i must be brought in at low energy. The resulting values are listed in Table I. The error bars are estimated from the experiment as well as from the fitting procedure. In the thinnest layers Δk_i is far from the hole lifetime contribution, which should be lower than 0.02 $Å^{-1}$.[18] On the other hand, the thickness dependence suggests the influence of confinement inside the quantum well.[19] This leads to wave vector broadening via the uncertainty principle. In our case $1/d$ ranges from 0.185 $Å^{-1}$ to 0.093 $Å^{-1}$ for 3.0 to 6.0 ML. The experimental Δk_i values listed in Table I lie within the same order of magnitude and roughly reproduce the decreasing trend from 3 ML to 6 ML. However they clearly fall short compared with $1/d$. A possible explanation could be a significant penetration of the QW wave function inside the Co band gap, such that the effective QW thickness is actually larger.[20] Indeed our QW states lie very close to the edge of the minority-spin band gap (nominally[3] at -0.7 eV below E_F); thus a large penetration is expected. At the same time, the strong wave function tailing inside Co can result in an effective smoothening of the interface step barrier. The smoothing of the interface and the surface potential barriers, either due to electronic effects or to roughness, can explain the absence of large final-state surface-interface interference effects, such as those observed in other thin films.[7,8]

In summary, we have studied the photoemission cross section in thin Cu films in a wide energy range. We observe a periodic behavior in the reduced wave vector scale, with peaks at the QW state $k_\perp$. The peaks in the cross section curve have been analyzed in terms of initial- and final-state wave vector broadening. Initial-state broadening is determined only at the lowest-energy range, due to the noticeable reduction in final-state broadening. The values obtained for Δk_i as well as its thickness dependence indicate that initial-state broadening is linked to confinement within the film (via the uncertainty principle) rather than to photohole lifetime, which should be the dominating effect in thicker films.

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[19] For a two-dimensional system one has to consider two different contributions to $\Delta k_\perp$ in the initial state, i.e., the photohole lifetime and electron confinement within the QW. For sharp confinement the latter can be the dominant broadening effect, as shown in surface states (Ref. 14).
[20] A more accurate uncertainty relation can be obtained from the analytical expression of the quantum well wave function, including the part that tails inside the Co crystal. To this aim, further theoretical work is currently being undertaken.